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CO_2 as a fracturing fluid: Potential for commercial-scale shale gas production and CO_2 sequestration

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Abstract

Hydraulic fracturing and horizontal drilling has led to a shale gas energy boom in the United States. In addition to decreasing domestic energy costs, shale gas production has substantially reduced domestic CO_2 emissions, largely due to natural gas displacing coal-fired electricity generation. Water is the principal component of working fluids used for commercial hydraulic fracturing, along with other constituent chemicals and substances to enhance fracture propagation/longevity and propping agent (e.g., sand) transport. Industry, policy makers, and other stakeholders are aware of potential disadvantages of aqueous fracturing fluids, including water scarcity, environmental impact from constituent chemicals, and poor fracture performance. To address these problems we are undertaking a study using supercritical CO_2 as a replacement working fluid. Supercritical CO_2 has many potential benefits and drawbacks compared with water as a fracturing fluid; it may increase gas production through several coupled processes including enhanced fracturing, reduced flow blocking, and miscibility with in-place hydrocarbons, as well as challenges such as economics, resource availability, and assurances that the CO_2 is safely sequestered in the target formation. Through a combination of basic experiments, modelling, and historical research, we formally address these issues.

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Keywords: Shale gas, hydraulic fracturing, supercritical CO_2

1. Introduction

Supercritical CO_2 (sCO_2) is a promising alternative to water for shale gas fracturing. Los Alamos National Laboratory (LANL) is leading a three-year multi-million dollar research project that compares the production effectiveness, economics, and environmental impact of shale gas production using supercritical sCO_2 and water. The

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project is a collaboration between LANL, several universities, and a leading shale gas exploration company. A key focus of the study is to understand how CO_2 is sequestered during the fracturing process while simultaneously increasing the effectiveness of shale gas production and reducing the environmental footprint. Preliminary results from the project suggest that the combination enhanced fracturing and gas production, coupled with CO_2 storage potential, is sufficient to justify using sCO_2 to extract shale gas.

Previous studies have used sCO_2 as a fracturing fluid with encouraging results. For instance, a DOE-sponsored experiment, conducted before the hydraulic fracturing boom, showed that using sCO_2 resulted in up to five times more gas production compared to aqueous fluids, required no additives, and greatly minimized water usage. However, the experiments did not produce consistently positive results or identify the physical processes that led to the enhanced production. In addition, the experiments did not focus on the CO_2 sequestration potential. This project is directly addressing these key issues.

The project has developed a preliminary Monte Carlo-based framework—founded on a combination of basic science experimentation, modeling, and actual injection/production data—to understand and quantify the differences between sCO_2 and water as fracturing fluids, with a particular focus on CO_2 storage potential. We have developed and tested several key hypotheses for how sCO_2 could outperform aqueous fracturing fluids, as well as some potential drawbacks. Prominent advantages for CO_2 include increased methane (CH_4) and other hydrocarbon production due to enhanced fracturing (e.g., strong Joule-Thompson cooling effect), reduced pressurization requirements at the well pad, displacing gas from lower-porosity fractures, reduced pore blocking, desorption of CH_4 from organic inclusions (CO_2 preferentially adsorbs onto shale), heavier hydrocarbons becoming miscible with the CO_2, straightforward separation of gelling and propping agents, and the elimination of injection and flow-back water. A common theme to these processes is the increased sequestration of CO_2 during the fracture process. For example, understanding how to increase CH_4 production through desorption is synonymous with increasing CO_2 storage. Potential drawbacks include the increased expense of capturing-pressurizing-transporting sCO_2, comprehensively accounting for the fate of the sCO_2, extracting the hydrocarbons from the flow-back CO_2, and separating/re-pressurizing the flow-back CO_2.

The framework is driven by physics-based process models that represent the different processes for injecting sCO_2 and water, generating/propagating fractures, extracting CH_4 and heavier hydrocarbons from the shale formation, and removing hydrocarbons and additives from the flow back sCO_2 and water. The physics for each sub-model have been developed, calibrated, and validated using combination of bench-scale experimentation and high-performance computer models. However, uncertainty is inherent in the process models since they cannot be validated in the field. Consequently, the framework incorporates a Monte Carlo approach to understand the impact of this uncertainty. This approach can be used to assess the sensitivity of model assumptions as well as identify areas where uncertainty must be reduced if sCO_2 shale gas is to become a commercial reality. Understanding the long-term fate of injected CO_2 that does not flow back (i.e., potentially sequestered CO_2) is a project priority. The framework can also be used to explore the impact of physical parameters (e.g., shale organic content, depth) and operational parameters (e.g., horizontal well length, cost of CO_2) in determining the potential for shale gas production while simultaneously sequestering CO_2.

We demonstrate the framework by presenting preliminary results based on two key shale gas formations. These results suggest that sCO_2 as the working fluid enhances shale gas enough to justify large-volume CO_2 purchases, particularly in the case where there is a moderate tax on CO_2 emissions. As a consequence, we suggest that sCO_2-based shale gas production has significant potential to drive the capture and storage of CO_2 at commercial scales.

2. CO_2 as a fracturing fluid

CO_2 has been used as a fracturing fluid with some encouraging results. In DOE sponsored experiments, conducted before the hydraulic fracturing boom, CO_2 resulted in up to five times more gas production compared to aqueous fluids, required no additives, and greatly minimized water usage, but did not produce consistently positive results. Lack of water, the need for deep disposal wells, and a growing belief that more stringent fracturing regulations are

pending has renewed interest in CO_2. One recent report states that CO_2-based fluids provide an interesting, although as yet unproven, possibility for enhancing gas recovery, reducing water required, and sequestering CO_2. Attractive attributes of CO_2 include the following. Under *in situ* conditions CO_2 is a supercritical fluid ($scCO_2$) exhibiting favorable miscibility with hydrocarbons, which makes it useful in enhanced oil recovery. Unlike water, hydrocarbon miscibility helps prevent flow blocking in small pores. CO_2 can also actively exchange with methane adsorbed in the shale[16]. In addition, biocides, surfactants, scale inhibitors and many other fracturing-fluid additives may be unnecessary if $scCO_2$ is used as the working fluid. However, an increase in viscosity may be required if $scCO_2$ must carry proppant. $scCO_2$ may also more effectively fracture rock due to coupled compressibility-thermal shock effects. Specifically, strong Joule-Thompson cooling may enhance rock fracturing due to thermal stress created as CO_2 expands into a new fracture volume and cools the crack tip.

3. Adsorbed gas

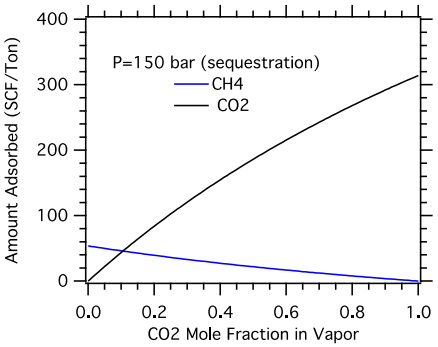

Fig. 1. Adsorption isotherms under sequestration-like conditions using experimentally determined Langmuir adsorption parameters..

We have compared a few basic aspects of $scCO_2$ and water in small pores. Analysis of shale samples obtained in the field has shown that a substantial fraction of the naturally existing porosity consists of pores with characteristic diameters in the nanometer to tens-of-nanometer range.[1-3] However, the overall porosity suggests that much of the methane gas contained in shale must be adsorbed under in-situ reservoir conditions. If CO_2 could preferentially replace methane on those surface sites, methane production could be increased. Also pumping CO_2 into the formation following the production phase could offer significant carbon sequestration potential. We performed an initial assessment of these issues using recently reported CO_2 and CH_4 adsorption data in shale[4] that clearly shows the propensity for CO_2 to adsorb onto shale (Fig.1). Langmuir adsorption parameters deduced from these single gas adsorption measurements were used in a multi-component extension of the Langmuir adsorption isotherm.[5] Assuming the shale formation is ultimately pressurized with CO_2 to 150 bar, 2175 psi, the calculations suggest that as much as 300 standard cubic feet (SCF) of CO_2 could be adsorbed per ton of shale. Thus, a fully accessible shale seam 1000m by 300m by 20m could potentially adsorb and sequester up to 1.7×10^7 SCF of CO_2. While these initial calculations are very encouraging, refinements are clearly required to provide quantitatively accurate assessments. For example, the Langmuir model assumes the heat of adsorption is identical for each surface adsorption site, there are no interactions between the adsorbed species, and ignores non-idealities in the fluid phase. Also, imperfect connectivity between induced and existing fractures will expectedly result in regions that are effectively inaccessible for sequestration purposes.

4. Surface tension

In nanometer scale pores, surface tension (capillary effects) may dominate fluid transport. The capillary number, which ratios the viscous and surface tension forces, provides a measure of which force dominates. Estimated capillary numbers in shale are well below 10^{-5} indicating that surface tension forces will likely dominate fluid transport. To provide some insight into what may happen with water based fracturing fluids, we considered the following simple situation. A straight cylindrical pore initially filled with liquid hydrocarbon was assumed to connect a water-filled induced fracture to a larger heavy (liquid) hydrocarbon reservoir. During fracturing, the water pressure must exceed the reservoir pressure, which pushes water into the cylindrical pore. A $\Delta P \sim$ 100 bar, 1450 psi, net pressure was assumed during fracturing. In the subsequent production mode the injected water pressure is reduced and water is (partially) removed as flow-back. At this point, it was assumed that the induced fracture was predominately filled with desorbed methane. Furthermore, the pressure of the hydrocarbon reservoir now exceeds that found in the induced fracture. If one assumes that ΔP is now ~50 bar but in a direction opposite to what existed during fracturing, one might expect that the hydrocarbons in the reservoir would flow through the pore and into the induced fracture network. However, a simple force balance calculation incorporating surface tension forces shows that water forced into in pores during the production mode effectively blocks the pore for all diameters less than ~35 nm, which includes a substantial fraction of the porosity in a typical shale. That is, the assumed pressure difference during production is not enough to overcome the surface tension forces holding the pore water in place. This blocking effect should not occur using miscible CO_2, highlighting one potential advantage.

5. Enhanced fracturing

Newly formed fractures instantaneously create void space, which the fracturing fluid subsequently fills. While filling of newly created voids with fluid is expected to take place over small time-scales, important differences in dynamic behavior may occur depending on whether the fracturing fluid is water or $scCO_2$. The differences originate from the thermo-physical properties of the two fluids. Of particular interest is the temperature change resulting from isenthalphic expansion, i.e. a Joule-Thompson throttling process.[6] As a preliminary calculation, we employed the Peng-Robinson equation of state (known to be accurate for sc-fluids) to estimate temperature changes upon isenthalpic expansion of both pure water and pure $scCO_2$ from reservoir conditions into a void space. Virtually no change in temperature was seen in water upon expansion down to pressures as low as 100 psia. However, $scCO_2$ partially liquefied and cooled on the order of 200°C when the pressure was lowered by the same amount. During this expansion the prospect of creating a thermal shock at the crack tip thus exists, which could promote additional fracture propagation. Of course, fracturing pressure will ultimately be re-established within the newly created fracture. However, during the transient low-pressure period, reduced temperatures could have beneficial effects on crack propagation provided enough heat can be transferred quickly from the crack tip to the cool fluid.

6. Discussion

Our preliminary work suggests that supercritical CO_2 has the potential to be commercially viable option for shale gas and oil production. Supercritical CO_2 has the ability to simultaneously reduce CO_2 emissions to the atmosphere through sequestration while enhancing gas extraction from unconventional resources. Interestingly, unlike enhanced oil recovery, efforts to maximize CO_2 sequestration will almost certainly increase oil and gas production. However, it is clear that significant further research is required.

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